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(54) **Solid component of a catalyst for the (co)polymerization of ethylene.**

(57) A solid component of a catalyst for the (co)polymerization of ethylene which comprises a silica carrier and a catalytically active portion including titanium, magnesium, chlorine and alkoxy groups is obtained by suspending activated silica in a solution of magnesium chloride and titanium tetraalcoholate in a liquid aliphatic acid ester; eliminating the aliphatic acid ester from the resulting suspension to recover a solid; and reacting the resulting solid with an alkyl aluminium chloride.

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The present invention relates to a solid component of a catalyst, the process for its preparation and its use in the polymerization of ethylene and the copolymerization of ethylene, preferably with alpha-olefins.

It is known that ethylene, or generally alpha-olefins, can be polymerized at low pressure with Ziegler-Natta catalysts. These catalysts are usually composed of a compound of elements from subgroups IV to VI of the periodic table (transition metal compounds), mixed with an organometallic compound, or hydride, of the elements of groups I to III of the periodic table.

Catalysts are also known in the art, in which the transition metal compound is supported on a solid carrier, either organic or inorganic, and sometimes physically and/or chemically treated. Examples of such solid carriers are the oxygenated compounds of bivalent metals (such as oxides, inorganic oxygenated salts and carboxylates) or hydroxychlorides or chlorides of divalent metals.

Solid components of catalysts are already known in the art which are obtained by activating a complex containing magnesium, titanium, halogen, alkoxy groups and an electron donor with an aluminium halide. This complex can be deposited on a porous carrier and then activated, thereby affording solid catalyst components which are particularly suitable for the homo-or copolymerization of ethylene in the gas phase. This technique is described, e.g., in US-A-4,354,009, 4,359,561, 4,370,456, 4,379,758 and 4,383,095.

These supported catalysts allow the production of polyethylene in a flowing granulated form. Problems often arise, however, caused by the limited rheology of the polymer due to the presence of fines and the friability of the granules. Another problem is the low productivity, referring to the quantity of polymer which can be obtained per weight unit of catalyst.

It is now been found that it is possible to obtain solid components of Ziegler-Natta catalysts on a carrier prepared from particulate (microspheroidal) silica and a solution of magnesium chloride and titanium alcoholate in an aliphatic acid ester, using a simple and convenient procedure which affords solid catalyst components having an improved catalytic activity in the (co)polymerization of ethylene and being capable of yielding polyethylene of satisfactory rheology.

Accordingly, the present invention provides a process for the preparation of a solid component of a catalyst for the (co)polymerization of ethylene, comprising a carrier of silica in the form of particles (50-90% by weight) and a catalytically active portion (50-10% by weight) including titanium, magnesium, chlorine and alkoxy groups. Said process comprises the following steps:

(a) preparing a solution of titanium tetraalcoholate of formula $Ti(OR)_4$ wherein the groups R independently represent linear or branched alkyl radicals containing from 1 to 5 carbon atoms,and of magnesium chloride in a liquid aliphatic acid ester, the molar ratio of titanium tetraalcoholate to magnesium chloride ranging from 0.2/1 to 5.0/1;

(b) impregnating silica in particle form with the solution prepared in step (a) by suspending the silica particles in said solution;

(c) eliminating the ester from the suspension obtained in step (b) by means of evaporation at a temperature which does not exceed 60°C and recovering a solid composed of silica particles onto which a complex of formula $Ti(OR)_4 \times (0.2\text{-}5.0)MgCl_2$ is deposited;

(d) reacting the solid obtained in step (c) with alkyl aluminium chloride, at an operating temperature of from about 10 to about 100°C and for about 10 minutes to about 24 hours; and

(e) recovering the solid catalyst component.

Preferably, a silicon halide is also added to the solution obtained in step (a), usually in such quantities as to afford an atomic ratio of silicon, in the silicon halide, to titanium, in the titanium tetraalcoholate, of from 0.5/1 to 8.0/1. It is even more preferred to add the silicon halide in amounts such as to result in a Si/Ti ratio of from 2.0/1 to 6.0/1. The use of the silicon halide further improves the activity of the catalyst.

According to the process of the present invention, a solution of titanium tetraalcoholate and magnesium chloride in a liquid aliphatic acid ester is prepared in step (a). Specific examples of titanium tetraalcoholates suitable for this purpose are titanium tetra-n-propylate, titanium tetra-n-butylate, titanium tetra-i-propylate and titanium tetra-i-butylate. The magnesium chloride to be employed is preferably a totally anhydrous, or almost totally anhydrous (water content less than about 1% by weight) magnesium chloride. The liquid aliphatic acid ester preferably is selected from methyl,ethyl and propyl esters of lower (e.g. C_1-C_4) aliphatic carboxylic acids, chlorinated or non-chlorinated, such as ethyl formate, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate and ethyl chloroacetate. The most preferred ester is ethyl acetate. It is convenient to use solutions having a total concentration of titanium tetraalcoholate and magnesium chloride of about 4 to 10% by weight and the molar ratio of titanium tetraalcoholate to magnesium chloride preferably is in the vicinity of or equal to 1:1 (e.g. 1.2:1 to 1:1.2).

The silicon halide - if employed - is preferably selected from silicon tetrahalides and halosilanes. Specific examples of such compounds are silicon tetrachloride, trichlorosilane, vinyl trichlorosilane, trichloroethoxy silane and chloroethyl trichlorosilane. Silicon tetrachloride is particularly preferred.

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Preferably the solution of step (a) is prepared by dissolving the components in the aliphatic acid ester at room temperature or above, if possible at the reflux temperature of the ester used.

In step (b) of the process of the present invention silica particles are impregnated with the solution prepared in step (a) by suspending the silica particles in the solution. For this purpose, microspheroidal, porous silica is preferable, said silica having a particle size of from 10 to 100 µm, a SiO_2 content of >90% by weight, a surface area of from 250 to 400 m^2/g, a pore volume of from 1.3 to 1.8 ml/g and an average pore diameter of from 20 to 30 nm. Preferably, this silica has undergone an activation treatment prior to the impregnation, which treatment can be carried out, e.g., by heating the silica in an inert atmosphere, at a temperature of from about 100 to about 650 °C, over a period of from 1 to 20 hours, or by contacting the silica with an organometallic compound, such as an alkyl magnesium or alkyl aluminium compound, e.g., butyl magnesium, octyl butyl magnesium and triethyl aluminium, operating at room temperature or at higher temperatures, for example at about 60 °C. It is preferred to activate the silica by treatment with octyl butyl magnesium, e.g., in quantities of about 10 to 20% by weight of silica. The impregnation of step (b) is preferably carried out at a temperature of from about 50 to about 75 °C, over a period of from about 0.5 to about 5 hours.

In step (c), the ester is eliminated from the suspension obtained in step (b) by means of evaporation and a solid of silica particles is recovered onto which a complex of titanium tetraalcoholate and magnesium chloride in a molar ratio of from 0.2/1 to 5.0/1, preferably about 1:1, depending on the quantity used in step (a), is deposited. The evaporation of the aliphatic acid ester should be carried out at a temperature which does not exceed 60 °C, optionally at a reduced pressure. Total evaporation of the ester is not necessary and at the end of step (c) it may still be present in quantities of up to 20% by weight, preferably not more than about 5 to 10% by weight, with respect to the weight of the magnesium chloride.

In step (d) of the present process, the solid obtained in step (c) is reacted with alkyl aluminium chloride, the atomic ratio of chlorine atoms, in the alkyl aluminium chloride, to alkoxy groups, in the titanium alcoholate, preferably ranging from 0.5/1 to 7.0/1. More specifically, in step (d), the solid is suspended in an inert liquid hydrocarbon such as hexane or heptane, and is contacted with an alkyl aluminium chloride, generally selected from diethyl aluminium chloride, ethyl aluminium sesquichloride, diisobutyl aluminium chloride and isobutyl aluminium dichloride, dissolved in the above hydrocarbon solvent or in a different hydrocarbon solvent. Step (d) is carried out at a temperature ranging from about 10 to about 100 °C, for a period which, depending on the chosen operating temperature, usually varies from about 10 to about 24 hours. The preferred operating temperature ranges from about 20 to about 90 °C, over a period of about 10 minutes to about 1 hour, and the preferred atomic ratio of chlorine to titanium in the solid ranges from 2/1 to 14/1. This treatment has the effect of increasing the chlorine content in the solid catalyst component, with a simultaneous reduction, either partial or total, of the titanium from the tetravalent state to the trivalent state, and with the partial or total elimination of the alkoxy groups present.

At the end of the treatment, the solid catalyst component is recovered in step (e), is preferably washed with a liquid aliphatic hydrocarbon solvent, such as hexane or heptane, until the chlorides have been eliminated from the washing liquid, and is finally dried.

The solid catalyst component according to the present invention is composed of a particulate silica carrier (50-90% by weight) and a catalytically active portion (50-10% by weight) including titanium, magnesium, chlorine and alkoxy groups. A preferred catalyst component also contains silicon, the ratio Si/Ti preferably ranging from 0.5/1 to 8.0/1, particularly from 2.0/1 to 6.0/1.

The present invention also provides a catalyst for the (co)polymerization of ethylene, comprising the above solid catalyst component, combined with an organometallic compound of aluminium (co-catalyst), preferably chosen from aluminium trialkyls and alkyl aluminium halides (particularly chlorides), containing from 1 to 5 carbon atoms in the alkyl groups. Among these, aluminium trialkyls with from 2 to 4 carbon atoms in the alkyl groups, such as triethyl aluminium, tributyl aluminium and triisobutyl aluminium are particularly preferred. The catalyst of the present invention has an atomic ratio of aluminium (in the co-catalyst) to titanium (in the solid component of catalyst) which generally ranges from 20:1 to 250:1, preferably from 100:1 to 200:1.

The catalyst of the present invention can be used in polymerizations carried out by means of the suspension technique in an inert diluent or by using the gas phase method in a fluidized or stirred bed. Alpha-olefins which can be copolymerized with ethylene are generally those containing from 3 to 10 carbon atoms, preferably from 4 to 6 carbon atoms, such as butene-1, hexene-1 and 4-methyl-pentene-1. The general polymerization conditions are: temperature of from about 50 to about 100 °C; total pressure of from about 5 to about 40 bar, the ratio of partial pressures of hydrogen and ethylene being from 0 to about 10. There is obtained, at any rate, a high productivity in the olefinic polymer and the polymer thus obtained has excellent rheological properties and, in particular, is in the form of granules which are non-friable and do not

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contain fines.

In the following non-limitative examples which are intended to provide a better understanding of the present invention, a microspheroidal silica carrier is used, said carrier having a particle size ranging from 20 to 60 µm, a SiO_2 content of >99% by weight, a surface area of 320 m^2/g, a pore volume of 1.65 ml/g and an average pore diameter of 25 to 26 nm.

EXAMPLE 1

6.60 g (19.4 mmoles) of titanium tetra-n-butylate, 1.87 g (19.6 mmoles) of anhydrous magnesium chloride and 150 ml of anhydrous ethyl acetate are charged, in a nitrogen atmosphere, into a 250 ml flask equipped with reflux cooler, mechanical stirrer and thermometer. The mixture is heated to reflux (about 77°C) for 1 hour to allow the complete dissolution of the magnesium chloride.

11.4 g of microspheroidal silica, previously activated by contacting it, for 1 hour at 60°C, with a solution containing 150 ml of anhydrous n-hexane and 13 ml of 20% by weight of octyl butyl magnesium in heptane, are suspended in the solution thus obtained. The suspension is kept at a temperature of 60°C for 1 hour whereafter it is dried by evaporating the solvent at a temperature not higher than 60°C and at reduced pressure. Thereby a solid is recovered onto which the complex $Ti(OBu)_4.MgCl_2$ has been deposited.

The solid thus obtained is suspended in 70 ml of anhydrous n-hexane, and 18 ml of a 40% by weight solution of ethyl aluminium sesquichloride (6.08 g; 23.6 mmoles) in n-decane are added to the resulting suspension. Contact is maintained for 15 minutes at a temperature of 25°C. The solid is then recovered by filtration, washed with anhydrous n-hexane until all the chlorides in the washing liquid have been eliminated, and finally dried at reduced pressure.

A solid catalyst component is thus obtained, in solid granule form, which contains 70% by weight of silica and the catalytically active portion whereof contains magnesium, titanium, chlorine and butoxy groups in a molar ratio of 2.2:1.0:5.3:0.4.

The solid catalyst component prepared in the above way is used in a test for the polymerization of ethylene. More specifically, the polymerization is carried out in a 5 litre autoclave containing 2 litres of n-hexane. The process is carried out at a pressure of 15 bar, in the presence of hydrogen (the pressure ratio of hydrogen to ethylene being 0.47/l), at a temperature of 90°C and over a period of 2 hours, using 150 mg of the solid catalyst component and triethyl aluminium as co-catalyst, the atomic ratio of aluminium in the co-catalyst to titanium in the solid catalyst component being 50/l.

A yield equal to 3.8 kg of polyethylene per gram of solid catalyst component is thus obtained and the polyethylene has the following characteristics:

- density: 0.961 g/ml
  (ASTM D-1505)
- apparent density: 0.38 g/ml
  (ASTM D-1895)
- MFI (2.16 kg): 2.5 g/10'
  (Melt-Flow Index - ASTM D-1238)
- MFR: 31.4
  (MFR = Melt-Flow Index Ratio, defined as the ratio MFI (21.6 kg)/MFI (2.16 kg)).

The polyethylene is in granule form with the following size distribution in µm:

≥2000	0.1% by weight
<2000 to ≥1000	2.8% by weight
<1000 to ≥ 500	78.2% by weight
< 500 to ≥ 250	17.4% by weight
< 250	1.5% by weight.

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EXAMPLE 2

6.60 g (19.4 mmoles) of titanium tetra-n-butylate, 1.87 g (19.6 mmoles) of anhydrous magnesium chloride, 150 ml of anhydrous ethyl acetate and 9.0 ml of silicon tetrachloride (13.2 g, 77.8 mmoles) are charged, in a nitrogen atmosphere, into a 250 ml flask equipped with reflux cooler, mechanical stirrer and thermometer. The mixture is heated to reflux (about 77°C) for 1 hour to allow the complete dissolution of the magnesium chloride.

11.4 g of microspheroidal silica previously activated by contacting it, for 1 hour at 60°C, with a solution containing 150 ml of anhydrous n-hexane and 13 ml of 40% by weight octyl butyl magnesium in n-heptane, are suspended in the solution thus obtained. The suspension is kept at a temperature of 60°C for 1 hour whereafter it is dried by evaporating the solvent at a temperature not higher than 60°C and at reduced pressure. Thereby a solid is recovered onto which the complex $Ti(OBu)_4.MgCl_2$ is deposited.

The solid thus obtained is suspended in 70 ml of anhydrous n-hexane and 18 ml of a 40% by weight solution of ethyl aluminium sesquichloride in n-decane (6.08 g; 23.6 mmoles) are added to the resulting suspension. Contact is maintained for 15 minutes at a temperature of 25°C. The solid is then recovered by filtration, washed with anhydrous n-hexane until all the chlorides in the washing liquid have been eliminated, and finally dried at reduced pressure.

A solid catalyst component is thus obtained, in solid granule form, which contains 70% by weight of silica and the catalytically active portion whereof contains magnesium, titanium, chlorine and butoxy groups in a molar ratio of 1.4:1.0:7.3:0.4.

The solid catalyst component prepared in the above way is used in a test for the polymerization of ethylene. More specifically, the polymerization is carried out in a 5 litre autoclave containing 2 litres of n-hexane. The process is carried out at a pressure of 15 bar, in the presence of hydrogen (pressure ratio of hydrogen to ethylene of 0.47/l), at a temperature of 90°C over a period of 2 hours, using 75 mg of the solid catalyst component and triethyl aluminium as co-catalyst, the atomic ratio Al/Ti being 100/1.

A yield equal to 6.6 kg of polyethylene per gram of the solid catalyst component is obtained and the polyethylene has the following characteristics:

- density:	0.961 g/ml
- apparent density:	0.31 g/ml
- MFI (2.16 kg):	3.3 g/10'
- MFR:	30.2

The polyethylene is in granule form with the following size distribution in µm:

≥2000	5.7% by weight
<2000 to ≥1000	45.8% by weight
<1000 to ≥ 500	45.0% by weight
< 500 to ≥ 250	2.6% by weight
< 250	0.9% by weight .

EXAMPLE 3

6.60 g (19.4 mmoles) of titanium tetra-n-butylate, 1.87 g (19.6 mmoles) of anhydrous magnesium chloride, 150 ml of anhydrous ethyl acetate and 4.5 ml of silicon tetrachloride (6.6 g; 38.9 mmoles) are charged, in a nitrogen atmosphere, into a 250 ml flask equipped with reflux cooler, mechanical stirrer and thermometer. The mixture is heated to reflux temperature (about 77°C) for 1 hour to allow the complete dissolution of the magnesium chloride.

11.4 g of microspheroidal silica, previously activated by contacting it, for 1 hour at 60°C, with a solution containing 150 ml of anhydrous n-hexane and 13 ml of 40% by weight of octyl butyl magnesium in n-heptane, are suspended in the solution thus obtained. The suspension is kept at a temperature of 60°C for 1 hour whereafter it is dried by evaporating the solvent at a temperature not higher than 60°C and at reduced pressure. Thereby a solid is recovered onto which the complex $Ti(OBu)_4.MgCl_2$ is deposited.

The solid thus obtained is suspended in 70 ml of anhydrous n-hexane, and 18 ml of a 40% by weight solution of ethyl aluminium sesquichloride in n-decane (6.08 g; 23.6 mmoles) are added to the resulting

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EUROPEAN SEARCH REPORT

Application Number

EP 91 11 7316

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	US-A-4 359 561 (WILLIAM A. FRASER) * claims 1,13,14,17 * * page 5, line 35 - line 46 * * page 6, line 1 - line 25 * * page 6, line 36 - line 69 * * page 7, line 23 - line 30 * * page 7, line 45 - line 53 * ---	1,4	C08F10/02 C08F4/655 C08F4/656
P,X	US-A-5 024 982 (GIL P. HAWLEY) 18 June 1991 * claims 1-3,10,14 * * page 2, line 8 - line 18 * * page 3, line 9 * * page 3, line 60 - page 4, line 16 * * page 5, line 7 - line 16 * * page 6, line 4 - line 66 * * page 5, line 25 - line 30 * ---	1,6	
P,X	EP-A-0 446 989 (MONTEDIPE) 18 September 1991 * claims 1-5,8-14 * -----	1-3,5,8,9,11-13	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 MAY 1992	FISCHER B.R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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P : intermediate document

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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